

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION

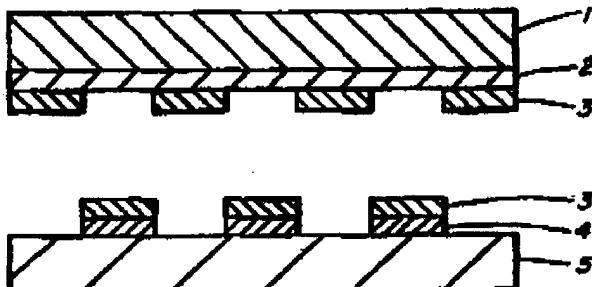
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5: C09J 4/06, 167/07		A1	(11) International Publication Number: WO 94/13749
			(43) International Publication Date: 23 June 1994 (23.06.94)
<p>(21) International Application Number: PCT/CA93/00519</p> <p>(22) International Filing Date: 13 December 1993 (13.12.93)</p> <p>(30) Priority Data: 07/990,289 14 December 1992 (14.12.92) US</p> <p>(71) Applicant: BANK OF CANADA (CA/CA); Dept. of Banking Operations, 234 Wellington Street, Ottawa, Ontario K1A 0G9 (CA).</p> <p>(72) Inventor: PINCUS, Alon, Hibbert; 9 Willard circle, Andover, MA 01810 (US).</p> <p>(74) Agent: POLE, Frank, L.; Gowling, Strathy & Henderson, Suite 2600, 160 Elgin Street, Ottawa, Ontario K1N 8S3 (CA).</p>			
<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TU).</p> <p>Published: With international search report.</p>			

(54) Title: THIN FILM SECURITY DEVICE (TFSID) APPLICATION PROCESS AND ADHESIVE THEREFOR



(57) Abstract

An ultraviolet (UV) radiation-curable temporarily pressure sensitive composition which when irradiated with ultraviolet light quickly attains a high tack state for transferring dielectric material thereto, and within hours permanently bonds to the dielectric material to form a thin film security device (TFSID). The UV radiation-curable pressure sensitive adhesive comprises, in one aspect: (a) at least one saturated copolyester having terminal acrylic double bonds and hydroxyl moieties; (b) at least one pigment dispersed in a liquid selected from the group consisting of an acrylic monomer, a vinyl ether monomer, oligomers thereof, and blends thereof; (c) at least one vinyl ether monomer, oligomers thereof, or blends of said vinyl ether monomer and oligomers; and (d) at least one photoinitiator in a quantity sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation. In another aspect the UV radiation-curable temporarily-pressure-sensitive adhesive is as described above with the exception that it is "clear", i.e. contains no pigment. The invention also provides a method of providing a substrate (and more specifically, banknote paper) with indicia, which comprises: (1) forming a laminate of (a) a polyester film having a thickness of 12-25 microns, (b) a release coating of a thickness of 1-3 microns, (c) a protective layer 1-2 microns thick, and (d) a stack of dielectric and/or metal layers having a maximum thickness of 1 micron; (2) providing a plurality of areas on the substrate, each of which areas bear a UV-curable pressure-sensitive adhesive as described above; (3) injecting the substrate containing the aforesaid adhesive-bearing areas to UV radiation to cause the areas to become highly tacky; (4) bringing the outer surface of the stack of dielectric and/or metal layers into pressurized contact with the adhesive-bearing areas on the substrate, thereby adhering the laminate to the adhesive-bearing areas on the substrate; and (5) stripping the laminate away from the substrate, whereby the dielectric and/or metal layers are sheared from the release coating and firmly adhere to said adhesive-bearing areas on the substrate.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	ME	Morocco
AD	Austria	GE	Georgia	MW	Macao
BB	Barbados	GN	Greece	MG	Mayer
BE	Belgium	GR	Hungary	ML	Moldova
BY	Belarus	HR	Iceland	MO	Norway
BG	Bulgaria	IE	Ireland	MZ	New Zealand
BA	Bosnia	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KZ	Kazakhstan	RO	Romania
CA	Canada	KG	Kyrgyzstan	RS	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	RU	Russia
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kuwait	SI	Slovenia
CI	City of Dakar	LK	Lithuania	SK	Slovakia
CO	Colombia	LK	Sri Lanka	SI	Singapore
CR	Costa Rica	LS	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CE	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Tobago and Tonga
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Malta	US	United States of America
EL	Greece	MM	Myanmar	UZ	Uzbekistan
FR	France			VI	Viet Nam
GA	Gabon				

- 1 -

THIN FILM SECURITY DEVICE (TFSD) APPLICATION PROCESS
AND ADHESIVE THEREFOR

FIELD OF INVENTION

The present invention relates to a combination of components to obtain a temporarily pressure-sensitive UV curable adhesive, and more particularly to a combination of components to obtain a printable pigmented temporarily pressure sensitive UV curable adhesive. Still more particularly, the present invention relates to formulations which can be printed as an ink, then become temporarily pressure sensitive adhesives upon exposure to ultraviolet light, attaining a high tack state for transferring dielectric material thereto, and within hours permanently bonds to the dielectric material to form a thin film security device (TFSD).

The application of dielectric material to valuable documents has been found to provide excellent security devices. The dielectric material is applied in a thin layer to the document by either a conventional labelling technique or a hot foil stamping technique.

Conventional labelling techniques involve a process wherein pressurized contact is used to bond the dielectric material to a suitable document or substrate. However, the proposed conventional labelling techniques have required elaborate transfer processes which in many cases do not provide a permanent bond between substrate and dielectric material. Furthermore, the dielectric film once bonded is relatively thick which can cause distortion of the document and handling problems.

SUBSTITUTE SHEET

WO 94/13749

PCT/CA93/00519

- 1a -

The present invention provides a unique pressure sensitive adhesive which permanently bonds a dielectric material in an uncomplicated room temperature conventional labelling technique to

SUBSTITUTE SHEET

- 2 -

provide a thin film security device of minimum thickness.

SUMMARY OF THE INVENTION

According to one aspect of the present invention there is provided an ultraviolet radiation curable temporarily pressure-sensitive adhesive composition comprising:

(a) at least one saturated copolyester having terminal acrylic double bonds and hydroxyl moieties;

(b) at least one polymerizable component selected from the group consisting of acrylic monomers, oligomers thereof, blends of said acrylic monomers and oligomers, and blends of said acrylic monomers or oligomers with a vinyl ether monomer;

(c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomer and oligomers; and

(d) at least one photoinitiator in a quantity sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, said adhesive composition being curable to a tack-free state within 24 hours.

The present invention also provides an ultraviolet radiation curable temporarily pressure-sensitive adhesive composition which comprises:

(a) at least one saturated copolyester with some terminal acrylic double bonds;

(b) at least one polymerizable component selected from the group consisting of acrylic monomers, oligomers thereof, blends of said acrylic monomers and oligomers, and blends of said acrylic monomers or oligomers with a vinyl ether monomer;

(c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomer and oligomers;

- 3 -

(d) at least one free radical photoinitiator and/or photosensitizer; and

(e) at least one cationic photoinitiator; the photoinitiator(s) being present in an amount sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, said adhesive composition being curable to a tack-free state within 24 hours.

According to the present invention in a further aspect there is provided a printable ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition which comprises:

(a) at least one saturated copolyester having terminal acrylic double bonds and hydroxyl moieties;

(b) at least one pigment dispersed in a liquid selected from the group consisting of an acrylic monomer, a vinyl ether monomer, oligomers thereof, and blends thereof;

(c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomers and oligomers; and

(d) at least one photoinitiator in a quantity sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, said adhesive composition being curable to a tack-free state within 24 hours.

The present invention also provides a printable pigmented ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition which comprises:

(a) at least one saturated copolyester with some terminal acrylic double bonds;

(b) at least one pigment dispersed in a liquid

WO 94/13749

PCT/CA93/00519

- 4 -

selected from the group consisting of an acrylic monomer, a vinyl ether monomer, oligomers thereof, and blends thereof;

5 (c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomer and oligomers;

(d) at least one free radical photoinitiator and/or photosensitizer; and

10 (e) at least one cationic photoinitiator; the photoinitiator(s) being present in an amount sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, said adhesive composition being curable to a tack-free state within 24 hours.

15 The printable pigmented UV radiation curable temporarily pressure-sensitive adhesive composition of this invention as described in the two immediately preceding paragraphs has the following properties:

20 (1) it is printable on a relatively smooth paper substrate with good edge definition and uniform ink thickness;

(2) it is effective as a high tack adhesive at a maximum coating thickness of 12 microns;

25 (3) it is activatable to a tacky state upon exposure to either a medium pressure mercury vapor electrode (125 to 700 W/inch) or microwave powered electrodeless (300 W/inch or 600 W/inch) UV lamps at speeds up to 900 ft./min. depending on the light intensity;

30 (4) it is curable to a tack-free state within 24 hours; and

(5) when cured, it is resistant to solvents and washing machine laundering, and is also resistant to abrasion, folding and crumpling.

- 5 -

Preferably the above-described adhesive composition is printable by an offset gravure process and has a viscosity near 20 poise at 25 degrees Centigrade. The dry film has an optical density greater than 1.4.

According to another aspect of the present invention there is provided a method of providing a substrate with indicia, which comprises:

(1) forming a laminate of

10 (a) a polyester film of a thickness of 12-25 microns;

(b) a release coating of a thickness of 1-2 microns;

(c) a protective layer 1-2 microns thick;

15 and

(d) a stack of dielectric and/or metal layers having a maximum thickness of 1 micron;

20 (2) providing said substrate with a plurality of areas, each bearing a printable pigmented ultraviolet radiation curable temporary pressure sensitive adhesive having the constitution and characteristics as set forth above;

25 (3) subjecting said substrate containing said adhesive-bearing areas to ultraviolet radiation to render said areas tacky;

30 (4) bringing the outer surface of said stack of dielectric and/or metal layers into pressurized contact with said adhesive-bearing areas on said substrate, thereby adhering said laminate to said areas on said substrate; and (5) stripping said laminate away from the substrate, whereby the dielectric and metal layers are sheared from the release coating and firmly adhere to said areas on said substrate.

35 The present invention further provides an article

- 6 -

of manufacture comprising:

5 a substrate, to selected areas on the surface of said substrate is permanently bonded a semi-transparent dielectric material, said bonding being by means of the printable ultraviolet radiation-curable temporarily pressure-sensitive adhesive having the constitution and characteristics as set forth hereinabove.

10 The present invention still further provides an article of manufacture which comprises a pattern of patches of semi-transparent dielectric materials and/or a very thin layer of metal, permanently bonded to banknote paper by means of a black UV radiation-curable temporarily pressure sensitive adhesive having the constitution and characteristics as set forth hereinabove.

15 The ultraviolet radiation-curable temporarily pressure-sensitive adhesive which comprises one aspect of the present invention comprises the following components:

20 (a) One or more saturated copolymers with some terminal acrylic double bonds and hydroxyl functionality. More specifically, the preferred polyester or blend of polyesters is that known under the tradename of "Dynacoll A", the exact composition of which is not known to the applicant; they are in the form of viscous liquids. Specific polyesters which have been found particularly useful in the present invention are those designated by the 25 tradenames "Dynacoll A 3130", "Dynacoll A 3170" and "Dynacoll A 3251". The "Dynacoll A" polyesters are saturated copolymers, which are partially terminally acrylated; having the following general structure:

30 $A_x - \text{saturated polyester} - B_y$
35 wherein A represents a group containing a double bond

- 7 -

reactive to energy-rich radiation; B represents a group non-reactive to radiation; and $x + y$ is equal to the functionality of the polyester. These polyesters are further characterized by having an average molecular weight from 3,000 to 6,000; and they have a large number of preferably branched alkyl side chains in the molecule, and have glass transition temperatures ranging from -10°C to -50°C. For a further description of these partially acrylated saturated polyester resins and how they may be employed in formulating pressure-sensitive adhesives, reference is made to the technical paper of Hans F. Huber and Hartmut Müller, entitled "Radiation Curable Polyesters for the Formulation of Pressure-Sensitive Adhesives", Radiation Phys. Chem., Vol. 33, No. 5, pp. 443-450 (1989), said publication being incorporated herein by reference.

(b) A carbon black pigment which is dispersed in an acrylate monomer. More specifically the carbon black pigment dispersion which has been found particularly effective is one known under the tradename "Pennco 9B1" which is a dispersion of carbon black pigments in trimethylolpropane triacrylate (TMPTA) at approximately 20% by weight pigment concentration.

(c) One or more vinyl ether monomers, such as for example 4-hydroxybutylvinylether (HBVE), cyclohexylvinylether (CHVE), and triethyleneglycol divinylether (DVE-3), or oligomers thereof, or blends of the aforesaid vinyl ether monomers and oligomers.

(d) One or more free radical photoinitiators and/or photosensitizers. Free radical photoinitiators which have been found to be effective are acetophenone derivatives such as 2-hydroxy-2-methyl-1-phenylpropan-1-one known by the tradename of "Darocur 1173", or

WO 94/13749

PCT/CAS3/00519

- 8 -

diethoxy acetophenone, or a blend of the first-mentioned acetophenone derivatives with a thioxanthone and an amine benzoate, known under the tradename of "Darocur 4043"; or an acetophenone derivative having 5 also amine functionality, specifically the compound 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone, known under the tradename of "Irgacure 369".

(e) One or more cationic photoinitiators. 10 Cationic photoinitiators which have been found to be effective are triaryl sulfonium salts of hexafluorophosphate, known by the tradenames "FX 512" and "Cyracure UVI 6990", and of hexafluoroantimonate, known by the tradename "Cyracure UVI 6974". A 15 cationic photoinitiator is not essential if an amine functionality is present in the free radical photoinitiator combination.

The above components of the printable UV radiation-curable temporarily pressure-sensitive adhesive composition of the present invention are employed in the following relative proportions, expressed in percentages by weight, based on the entire composition:

25	(a) Acrylated copolyester	50 - 60%
	(b) Carbon black pigment dispersion	11 - 15%
	(pigment concentration in the range of 2.2 - 3.0% of the total composition)	
30	(c) Vinyl ether monomer	18 - 38%
	(preferably in the range of 25.0 - 35.0%)	
	(d) Free radical photoinitiators	1 - 6%
	(e) Cationic photoinitiators	0 - 2%
35	(and 0 - 6% by weight, based on component (c)).	

If the UV radiation-curable temporarily-pressure-

- 9 -

sensitive adhesives of the present invention are "clear", i.e. containing no pigment, the amounts of reactive oligomers - component (a) and component (b) (unpigmented) - ranges from 60% to 80% by weight, and the amount of vinyl ether monomer (component (c)) may range from 15% to 26% by weight, based on the total composition.

5

To prepare the adhesive, the acrylated copolyester must be heated to allow dispensing into a tared container. Either the pigment dispersion or the vinyl ether or both are then added and blended, heating to 50°C as necessary to facilitate mixing. The rest of the ingredients can be added and mixed in at room temperature. The mixing may be effected by any suitable means known in the art.

10

15 The pressure-sensitive adhesive as described above is storage stable (ie. has a shelf life of at least 2 years.)

20

The pressure-sensitive adhesive is obtained by UV curing of saturated copolymers with some terminal acrylic double bonds and hydroxyl functionality, viz., component (a) of the foregoing composition; and it is the addition of vinyl ether monomers that cause further reaction with the adhesive to cause it to form a dry and permanent film. The "Dynacoll A" polyesters are designed to be applied to a substrate by hot melt apparatus, and upon cure to form permanently tacky films. The applicant has found that the addition of the vinyl ether monomer (component (c) to the saturated copolyester serves to dilute the copolyester adhesive so as to provide an adhesive viscosity low enough for printing application to banknote paper as described hereinafter while at the same time ensuring that sufficiently high tack is developed for the transfer step. In addition, after curing, the vinyl

25

30

35

WO 94/13749

PCT/CAN/00519

- 10 -

ether reacts with residual reactive groups of the copolyester to form a dry and durable film.

There are several factors that limit the concentration of certain components.

5 1. The adhesive composition for application to a substrate such as bank note paper must be printable. This places limits on the viscosity of the composition. If the formulation is too fluid, it will be absorbed by the paper substrate. If the 10 formulation is too viscous, it will not print cleanly, resulting in poor line resolution and scumming in non-image areas. The "Dynacoll" oligomers must be diluted with monomer(s) to reduce their viscosity to make them 15 printable. Monomers differ in their efficiency as diluents. The ratio of oligomer(s) to monomer(s) is targeted to obtaining the optimum application viscosity.

20 2. The composition must cure upon exposure to UV radiation (2 x 300 watts per inch) at 200 feet per minute. Cure speed is a function of formulation components, application thickness and UV intensity. Typically, the thinner the layer, the faster the cure speed and the higher the UV intensity the greater the potential cure speed. In terms of formulation 25 components, cure speed is dependent on the photoinitiator type and level, the colour, and the chemical structure of the oligomers and monomers. In a preferred application of the present invention the formulation is black and the level of black pigment is 30 determined by the desired optical density of the cured adhesive. If less black pigment is used, the optical density would be too low. The more black pigment which is used, the slower the cure speed. The "Dynacoll" oligomers are not high speed curing 35 materials. In order to achieve the desired cure

WO 94/13749

PCT/CA93/00519

- 11 -

speed, fast photoinitiators and/or fast curing monomers must be used. However, the fastest free radical curing monomers tend to produce harder polymers, which means, less tacky surfaces. We have therefore endeavoured to optimize the level of TMPTA (trimethylolpropane triacrylate) in order to balance cure speed with tack.

We have found that certain vinyl ether monomers are excellent diluents for "Dynacoll" oligomers, appear to improve cure speed and definitely play an important role in postcuring (cationic curing) of the final product. Again the limitations on the level of vinyl ether used is determined by desired composition viscosity.

3. The composition must be a temporary pressure sensitive adhesive to allow transfer of TFSM and then permanently bond the TFSM to banknotes. We have found that this requirement is met by a dual cure UV system. The free radical cure of "Dynacoll" oligomers results in a pressure sensitive adhesive. Postcuring, presumably by cationic cure, hardens the adhesive to yield a non-tacky, scratch resistant, durable product. The types and levels of monomer greatly affect the performance of the dual cure system. The type and level of photoinitiator plays an even greater role in overall performance. We have found that the dual cure is obtainable with a combination of free radical and cationic photoinitiators, but that the free radical photoinitiator has a greater effect. We have also found that the use of amine functional free radical photoinitiators eliminates the need for a cationic photoinitiator. Too much photoinitiator results in a drier initial surface than desired (poor transfer) and can result in a surface cure that prevents light penetration to the interlayer between the surface and

WO 94/13749

PCT/CA93/00519

- 12 -

the substrate (wetback on transfer film). Too little photoinitiator results in insufficient cure.

In terms of functional description of substrate to which the adhesive of the present invention can be applied, it has been specifically designed to be applied to the smoother side of banknote paper. We have found that much poorer application and transfer are obtained on the rougher side of the banknote. We have also found that excellent results are obtained when this adhesive is applied to very smooth and/or non absorbent surfaces such as supercalandered papers and plastic films.

While the UV radiation-curable temporarily-pressure-sensitive adhesive compositions according to preferred aspects of the invention as described hereinabove include a pigment (and more particularly a black pigment) to render the composition printable, the compositions of the invention in its broadest aspects need not necessarily include a pigment. Such adhesive compositions without the presence of a pigment would be "clear", and would not be printable, but otherwise have all the desirable characteristics of the UV radiation curable temporarily pressure-sensitive adhesives of the invention as previously described, viz. the adhesives are temporarily pressure-sensitive, and upon exposure to ultraviolet radiation become highly tacky within about 1 second and are curable to a tack-free state within 24 hours to yield a durable scratch-resistant surface.

We have attempted to arrive at a UV-curable pressure-sensitive adhesive composition suitable for purposes of the present invention by combining a saturated copolyester with terminal acrylate groups and hydroxyl functionality with polyisocyanates such as the "Mondur"™ products from Mobay or with amines

WO 94/13749

PCT/CA93/00519

- 13 -

such as the "Versamid™" products from Henkel; however, this resulted in a two-component system. The isocyanate (or the amine) could not be added to the copolyester until just prior to use and it was found 5 that the pot life of the adhesive was very short - probably not more than about 2 hours. It has been discovered that the claimed combination of vinyl ethers with acrylated saturated copolymers and the other components described herein, yields a single 10 phase, storage-stable, ultra-violet curable adhesive which has a shelf life of at least about 1 year. No reaction between the components of the adhesive composition occurs until exposure to ultraviolet (UV) 15 radiation (or possibly elevated temperatures). Once the adhesive system is exposed to UV radiation, a pressure-sensitive adhesive is immediately obtained, followed by a decrease in surface tack and hardening of the printed adhesive. With the use of the correct ratio of ingredients, the tack disappears within hours 20 and the material is scratch resistant and durable.

The UV radiation-curable temporarily-pressure-sensitive adhesive according to a preferred embodiment of the present invention has the following properties:

(1) It is black, and is characterized by having 25 an optical density greater than 1.4. The term "optical density", or opacity, is a measure of imperviousness to light, or the degree of opacity of a medium, expressed as $d = \log_{10} \frac{I_0}{I}$ where I_0 is the 30 intensity of incident light and I is the intensity of the reflected light.

(2) It is printable on a relatively smooth substrate, and in particular, on the smoother side of bank note paper, with good edge definition and uniform 35 ink thickness.

WO 94/13749

PCT/CAN/00519

- 14 -

(3) It is activated to a tacky state with the use of one or two 300W/inch UV lamps at a linear speed of up to 400 ft./min.

5 (4) It is capable of attaining a high tack state by ultraviolet radiation initiation in less than 1 second after exposure to ultraviolet radiation.

(5) It is effective as a high tack adhesive at a maximum coating thickness of 12 microns.

10 (6) It is curable to a tack free state within 24 hours.

(7) It is capable of attaining a final bond strength in less than 200 hours after pressurized transfer at 40 psi for 250 milliseconds under ambient conditions.

15 (8) It is stable to prolonged exposure to varying temperatures below 100°C and varying relative humidities.

20 (9) When cured, it is resistant to solvents and washing machine laundering, and also resistant to abrasion, folding and crumpling.

The viscosity of the adhesive in its non-activated state ranges from about 3500-5200 cps. at 20°C.

25 The thin film security device (TFSD) to which reference has been made earlier in this specification is a reflective surface which switches colour when a viewer observes it from different angles. Bank notes with the TFSD are easily identified as genuine but difficult to counterfeit.

30 The TFSD optical coating material is supplied as a very thin releasable layer deposited on a plastic carrier ribbon. The above-described adhesive is used to secure the coating to banknotes in the following manner: /A motif (patch) in adhesive ink, approximately 10 mm by 12 mm, is printed over the

WO 94/13749

PCT/CAS3/00519

- 15 -

lithographic background on the face of each banknote. Each note is then exposed to ultra-violet light to begin curing of the adhesive. The plastic carrier ribbon is then forced into contact with the printed adhesive motif as it cures. This application, under appropriate pressure, ensures the instant formation of a positive bond between all three elements: the optical coating, the adhesive, and the banknote. Separation of the plastic ribbon from the banknote releases a portion of the TFSD optical coating onto the banknote surface in the exact image of the printed motif.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic drawing of the laminate and substrate before application.

Figure 2 is a schematic drawing of the laminate and substrate after application.

Figure 3 is a plan view of a sheet of banknote paper to which an array of patches of UV radiation curable printable pressure-sensitive adhesive according to the present invention has been applied.

The invention in its various aspects will now be further described, with reference to the accompanying drawings. Referring now to Figs. 1 - 3 of the drawings:

The UV radiation curable pressure-sensitive adhesive (4) is applied to a substrate or a document (5) by an offset gravure printing process or other similar printing application. The adhesive (4) is applied in patches on the document (5) in the shape of the final transferred thin film security device. The substrate or document (5) is preferably banknote paper, but may be other suitable paper carriers which, if desired, could be calendered or plastic coated. The maximum thickness of the adhesive (4) applied is

WO 94/13749

PCT/CA93/00519

- 16 -

12 μm . Figure 3 illustrates a typical array of patches of the adhesive applied to a sheet of banknote paper.

After the adhesive (4) is applied to the substrate (5) it is subjected to ultraviolet radiation. When the adhesive is exposed to ultraviolet light the photoinitiators therein initiate the polymerization of the adhesive.

The polymerization of the adhesive advances it to a tacky state. The adhesive is able to attain a highly tacky state by the action of ultraviolet radiation in less than 1 second after treatment.

The thin film of transparent dielectric material is brought into contact with the adhesive. The dielectric material is one of three layers of a laminate. The three layers of the laminate are:

- a polyester film of a thickness of 12-25 μm (1);
- a release coating (2); and
- a stack of dielectric and/or metal layers having a maximum thickness of 1 μm (3).

The polyester film is comprised of polyethylene terephthalate, a readily available material sold under such trade designations as "Mylar", "Hostaphan"™ and "Melinex"™. The release coating may be of any suitable release material known in the art. A suitable thickness of the release coating is about 5 micrometres.

The dielectric material layers (3) are made up of five layers, the outermost layers of which are of zirconia (ZrO_2), a central layer also of zirconia, and sandwiched between the outer and innermost zirconia layers are two layers of silica, the total thickness of the combined layers of dielectric material being about 0.8 microns. Alternatively the dielectric material may be comprised of outer layers of metal,

- 17 -

between which is a layer of silica (SiO_2) or alumina (Al_2O_3). One of the metal layers is of aluminum, and the other is "Inconel" (trademark), a nickel based, heat- and oxidation-resistant alloy with approximately 5 13% chromium, 6% iron, and small amounts of manganese, silicon and/or copper.

The thin film security material (TFSM) which is used with a clear adhesive (viz the UV radiation-curable temporarily-pressure-sensitive adhesive 10 composition as previously described in page 2 herein which does not contain any pigment) is that known as metal-dielectric, i.e. that described in the last two sentences of the immediately preceding paragraph.

15 The aluminum layer in the metal-dielectric TFSM is effectively fully reflective so there is no optical requirement for a pigmented (preferably black) adhesive in this case, as there is for the semi-transparent all-dielectric TFSM (thin film security material).

20 The layered thin film stack as described above is deposited on a polyethylene terephthalate web (380 mm wide, 0.025 mm thick and 1700 metres long), in a vacuum roll coater manufactured by Ulvac Japan. Zirconia and silica are heated by electron beams of 25 approximately 20 kW power. The deposition thickness is controlled by varying the speed at which material is moved under the electron beam, the beam current, and the sweep patterns of the electron beams. Zirconia and silica are deposited in a single pass of 30 the web through the two deposition chambers in the roll coater.

Thin film security devices and their mode of operation are further described in Baird et al, U.S. Patent No. 3,858,977, dated January 7, 1975, and in 35 the paper entitled "Optically Variable Devices for Use

WO 94/13749

PCT/CA93/00519

- 18 -

on Bank Notes", by J. Rolfe, Proceedings of the International Society for Optical Engineering, SPIE, Vol. 1210, January, 1990, incorporated herein by reference.

5 The transfer process, which takes place at room temperature, brings the dielectric material (3) on the outer surface of the laminate material into pressurized contact with the adhesive patches (4) on the paper. The high tack adhesive (4) is of sufficient strength to exceed the combined release coat (2) holding strength and the dielectric material (3) shear strength. When the laminate material is stripped away, the shape of the thin film security device will shear out of the stack material around the edges of the adhesive patches (4), leaving the dielectric patch bonded to the paper, with part of the release coat (2) as the exposed surface.

20 A final bond strength is obtained in less than 200 hours after pressurized transfer at 40 psi for 250 milliseconds. The pressurized transfer can be done with transfer pads on a Thin Film Application and Conversion System (TACS). Furthermore, the bond is stable after transfer to temperatures varying below 100°C with varying relative humidities.

25 The Thin Film Application and Conversion System (TACS) is a horizontal process machine where stacked bank note sheets are fed in one end and move on a flat horizontal path through each of the process sections to exit in stacked format at the opposite end.

30 The sheet feeder is a 5000 sheet capacity unit manufactured by Autofeeds London Ltd., London, England. The sheets are stacked with the longitudinal axis of the individual bank notes parallel to the process axis of the machine. Sheets are stream fed in shingled fashion with the trailing edge of each sheet

WO 94/13749

PCT/CA93/00519

- 19 -

overlapping the leading edge of the following sheet. Sheets are guided against a side lay on the feed board by skewed tapes and fed to a registration stop for transfer to the sheet transport system.

5 The sheet transport system consists of an endless dual chain and sprocket system equipped with mechanical grippers running in a horizontal track mounted below the top surface of a transport table. The bank note sheets are held by the same grippers 10 throughout the application process and move in a "web like" stream with a 6 inch (152 mm) longitudinal pitch spacing between individual bank notes, maintained from sheet to sheet by overlapping leading and trailing edges in shingled fashion. The double thickness 15 caused by this overlapping is accommodated by the resilience of the printing and application rollers.

20 The printing system uses a gravure offset process to deposit a measured portion of the above-described printable adhesive as a small printed motif on the surface of each bank note. The etched gravure cylinder is charged with ink using a double doctor blade and ink well system manufactured by Inta Roto Co. The gravure cylinder transfers the adhesive ink to a relieved rubber offset cylinder. The offset 25 cylinder deposits the ink directly onto the note sheet as the sheet passes horizontally beneath it through the nip created with the matching impression cylinder mounted beneath the transport table. The offset and impression rollers are relieved to permit passage of 30 the transport system grippers.

The UV curing stage is manufactured by Fusion UV Curing System, Rockville, Maryland, USA. The bank note sheets are passed beneath the curing unit and exit to the TFSM application stage.

35 The adhesive begins curing on exposure to ultra-

WO 94/13749

PCT/CAN/06519

- 20 -

violet (UV) light. The curing time is a function of the duration of the exposure and the intensity of the light source.

5 Exposure to UV radiation takes place after printing and prior to the arrival of the bank note sheets at the application process. The curing system initiates a photochemical polymerization of the adhesive ink which changes in fractions of a second from a liquid to a highly tacky adhesive.

10 The thin film security material (TFSM), i.e. the laminate as previously described, is applied to the bank note sheets while the adhesive is tacky, and it bonds instantly to form TFSDs. The adhesive dries as the bank note sheets travel to the PAS delivery system.

15 The ultraviolet radiation is provided by ultraviolet lamps having an output power rating of a minimum of 600 watts per inch transverse to the path of travel of the bank note sheets through the TACS. 20 Suitable lamps for this purpose are two banks of Fusion Systems Corp. "D" lamps or equivalent.

25 The application stage consists of a plurality of disc shaped rotary application units stacked side by side across the width of the transport table. The outside circumference of each rotary application unit is contoured with raised pressure points similar to gear teeth. The pitch of the pressure points matches the longitudinal pitch spacing of the individual notes on each sheet (6 in.). The application units are 30 matched to an impression cylinder beneath the transport table which creates a nip to provide the required application pressure. The ribbons of TFSM are contained in a plurality of cassette type storage and handling units which are individually mounted 35 within each application unit. As the application

WO 9413749

PCT/CA93/08519

- 21 -

units rotate in synchronization with the velocity of the bank note sheets moving on the transport table, the ribbons wind in and out of each cassette while being drawn on a circular path covering the pressure points around the circumference of each application unit. The indexing action of each application unit moves a fresh portion of TFSM ribbon over each pressure point as that particular point rotates into contact with an adhesive motif on the bank note sheets passing through the nip.

The TACS forces the laminate or thin film security material (TFSM) ribbon into direct contact with the adhesive motif with sufficient force to cause a complete transfer of the TFSM material to the bank note surface, separates the TFSM ribbon from the surface, and indexes the ribbon to the next section of coating for application. The application device applies a contact force equivalent to the force produced by rolling line contact, the contact force being adjustable in a range of 100 to 1000 N with a mean operating force of 200 N, such as to provide optimum control of adhesive deposition and image density. The transport system delivers the bank note sheets to a stacker unit which is also manufactured by Autofeeds London Ltd. The stacker piles the sheets in stacks of up to 5000 sheets.

The patches of permanently bonded dielectric material provide a security device for which tampering, counterfeiting and copying of the substrate is made more difficult. For example, to photocopy the article with the attached dielectric material will result in an inaccurate copy. The dielectric material reflects coloured light such that the resulting copy will contain areas corresponding to the patches of dielectric material which will be distorted. Any

WO 94/13749

PCT/CA93/00519

- 22 -

attempt to tamper with or remove the dielectric material will damage the article by possibly tearing the document so that successful copying is not possible.

5 As previously indicated, the thin film security device (TFSD) produced in accordance with the present invention, which device incorporates a UV cured adhesive as previously described, must meet a number of requirements so that it is durable in use, that is, 10 so that the thin film security device (TFSD) will last at least as long as any bank note to which it is applied.

15 The fully cured adhesive (24 hours or more after application on banknotes) with a top layer of thin film material must survive the following mechanical and chemical tests without a significant amount of thin film being removed, the judgement being made visually. The allowable amount of thin film removal is less than 10%.

20 (i) Crumple test - (to evaluate the ability of a TFSD printed bank note to survive folding and creasing). The thin film adhesive layers are placed on a square piece of bank note 2.25 inches on a side. This piece is rolled into a cylinder, 25 fitted into a metal cylinder, then compressed inside the cylinder with a closely fitting piston using a specified weight as the compression force. The piece is removed from the cylinder, unrolled, moved through 90 degrees and replaced in the cylinder for another compression (a second 30 crumple). The adhesive-thin film layers must survive four crumples. The apparatus used in this test is commonly known as the IGT Crumple Tester. Crumpled specimens are compared with 35 existing exemplars from previous tests.

WO 94/13749

PCT/CAS3/00519

- 23 -

(ii) Abrasion Test - to evaluate the ability of a TFSD printed bank note to survive the surface abrasion encountered during circulation:

5 Using an abrasion testing device similar to the Taber Abraser, a test is performed first on an area of the specimen note not containing a TSFD, to establish the effect of abrasion on intaglio ink. Two abrasion intensities are established; the first corresponding to just noticeable wear of the intaglio ink, the second corresponding to obvious wear. Two TFSD specimens are then subjected to the same treatments using the Taber model 503 Abraser, testing is performed with Taber CS10 abrading wheels with a standard 250 gram loading. The test is run for 100 cycles, after which just noticeable wear of the intaglio print of the bank note has occurred. Abraded specimens are compared to existing exemplars from previous tests.

10

15

20

(iii) Laundering Test - to evaluate the ability of the TSFD printed note to withstand laundering:

25 Using a TFSD specimen secured to an article of clothing, the specimen is subjected to a normal hot wash laundering cycle using a powerful detergent. Samples are enclosed in shirt pockets and subjected to a normal hot wash cycle: 3/4 cup (approximately 170 ml) "Tide" detergent with bleach in 41 litres of water (0.4t) at 43°C for 10 minutes, followed by a ten minute rinse in 41 litres of water at 20°C, and a final four minute spin at room temperature.

30

35

WO 94/13749

PCT/CA93/00519

- 24 -

(iv) Chemical Resistance Test to evaluate the ability of a TFSO printed bank note to resist exposure to chemicals:

Specimen notes with a TFSO are immersed in the following chemicals for the times and temperatures specified, and allowed to dry in air. Samples (e), (f) and (g) were water rinsed to remove the chemical before drying.

- a) Tetrachloroethylene at 65°C for 2 hours.
- b) Acetone at 23°C for 2 hours.
- c) Ethyl alcohol 95% at 65°C for 2 hours.
- d) Gasoline, lead free, regular grade at 23°C for 2 hours.
- e) Sodium hydroxide 1% solution, aqueous, at 65°C for 15 minutes.
- f) Sulphuric acid, 5% solution, aqueous, at 65°C for 2 hours.
- g) Sodium hypochlorite, 0.6%, at 65°C for 2 hours.
- h) "Tide"™ detergent, 0.5%, at 65°C for 2 hours.
- i) Toluene at 65°C for 2 hours.

The cured adhesives of the present invention, and the TFSO incorporating same, passes all of the above tests.

Following are examples of the present invention.

Adhesive formulations were prepared by mixing together the following ingredients, in the proportions indicated, as expressed in Table 1:

TABLE 1

	<u>Ingredients</u>	<u>Example 1</u>	<u>Example</u>
2			
35	(a) "Dynacoll A3251"	53.67%	

WO 94/13749

PCT/CAS3/00519

- 25 -

54.41%

(b) "Pennco 9B1" 11.78%

11.95%

(c) HBVE 30.22%

5 30.66%

(d) "Darocur 4043"
(a free radical
photoinitiator blend) 2.60%

2.65%

10 (e) FX 512
(cationic photoinitiator) 1.73%
0.33%

Tests were run on the TACS using the formulations given in Table 1. Viscosities were measured just prior to testing and adjusted with the appropriate vinyl ether diluent where necessary. Each test run was first made with one bank of UV lamps and the machine speed was increased from 120 to 140 to 160 feet per minute; and then a second bank of UV lamps was turned on and the machine speed was decreased from 160 to 140 to 120 feet per minute. Results are shown in Table 2.

TABLE 2

25	Residual	Formulation	Print Quality	Transfer Quality			Tack After 5 days
				at speeds (ft. per min.)			
30				120	140	160	
	Example 1 tack		Pass	A/A	A/A	A/A	No
35	Example 2 tack		Pass	A/A	A/A	A/A	No

WO 94/13749

PCT/CAS/00519

- 26 -

TransferQuality

1B = single bank of UV lamps
2B = double bank of UV lamps A = acceptable

5 It has been determined from experiments which have been conducted that the tackier the acrylated polyester oligomer and the higher the content of such oligomer in the formulation the greater the initial tack of the adhesive; and simultaneously, the higher
10 the vinyl ether content, the lower the residual tack of the adhesive. The vinyl ether is an excellent viscosity reducer for the acrylated polyester oligomer. Experiments have also revealed that a
15 chemical environment leading to formation of cations from exposure of the adhesive to UV radiation is necessary, and it is preferred that UV curing of the adhesive be effected at a relative humidity below 51% in the curing chamber.

Furthermore, experiments which have been
20 conducted have shown that the adhesive formulations of the present invention having components (a) - (e) within the ranges of proportions previously set forth herein, including Examples 1 and 2, when applied to banknotes, passed satisfactorily the crumple test, abrasion test, laundering test and chemical resistance
25 test previously described.

While a number of embodiments of the present invention have been described hereinabove, it will be readily apparent to persons skilled in the art that variations and modifications thereof can be made
30 and/or are possible without departing from the spirit and scope of the invention. It is therefore our intention that the present invention not be limited only to what has been specifically described above, but that the invention cover all embodiments as come
35 within the scope of the claims which follow.

- 27 -

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition comprising:
 - 5 (a) at least one saturated copolyester having terminal acrylic double bonds and hydroxyl moieties;
 - (b) at least one polymerizable component selected from the group consisting of acrylic monomers, oligomers thereof, blends of said acrylic monomers and oligomers, and blends of said acrylic monomers or oligomers with a vinyl ether monomer;
 - 10 (c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomer and oligomers; and
 - (d) at least one photoinitiator in a quantity sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, said adhesive composition being curable to a tack-free state within 24 hours.
2. An ultraviolet radiation curable temporarily pressure-sensitive adhesive composition which comprises:
 - 25 (a) at least one saturated copolyester with some terminal acrylic double bonds;
 - (b) at least one polymerizable component selected from the group consisting of acrylic monomers, oligomers thereof, blends of said acrylic monomers and oligomers, and blends of said acrylic monomers or oligomers with a vinyl ether monomer;
 - 30 (c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomer and oligomers;
 - (d) at least one free radical photoinitiator

WO 94/13749

PCT/CA93/00519

- 28 -

and/or photosensitizer; and

(e) at least one cationic photoinitiator; the photoinitiator(s) being present in an amount sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, said adhesive composition being curable to a tack-free state within 24 hours.

3. A printable ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition comprising:

(a) at least one saturated copolyester having terminal acrylic double bonds and hydroxyl moieties;

(b) at least one pigment dispersed in a liquid selected from the group consisting of an acrylic monomer, a vinyl ether monomer, oligomers thereof, and blends thereof;

(c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomer and oligomers;

(d) at least one photoinitiator in a quantity sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, and said adhesive being curable to a tack-free state within 24 hours.

4. A printable pigmented ultraviolet radiation-curable temporarily pressure sensitive adhesive composition which comprises:

(a) at least one saturated copolyester with some terminal acrylic double bonds;

(b) at least one pigment dispersed in a liquid selected from the group consisting of an acrylic monomer, a vinyl ether monomer, oligomers thereof and blends thereof;

WO 94/13749

PCT/CA93/00519

- 29 -

(c) at least one vinyl ether monomer, or oligomers thereof, or blends of said vinyl ether monomer and oligomers;

5 (d) at least one free radical photoinitiator and/or photosensitizer; and

10 (e) at least one cationic photoinitiator: the photoinitiator(s) being present in an amount sufficient to render the composition tacky within about 1 second after exposure to ultraviolet radiation, said adhesive composition being curable to a tack-free state within 24 hours.

15 5. A printable ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 3 or claim 4 which has the following properties:

(1) it is printable on a smooth paper substrate with good edge definition and uniform ink thickness;

(2) it is effective as a high tack adhesive at a maximum coating thickness of 12 microns;

20 (3) it is activatable to a tacky state upon exposure to ultraviolet radiation (125 to 700 W/inch) at linear speeds up to 900 ft./min. depending on UV intensity; and

25 (4) when cured, it is resistant to solvents and washing machine laundering, and is also resistant to abrasion, folding and crumpling.

30 6. An ultraviolet radiation-curable temporarily pressure-sensitive composition according to any one of claims 1-4 wherein the copolyester comprises polyesters which are saturated in the main chain and have some terminal acrylic double bonds and hydroxyl moieties, said polyesters being further characterized by having an average molecular weight of from 3000 to

WO 94/13749

PCT/CAS/00519

- 30 -

6000 and a glass transition temperature in the range of from -10°C to -50°C.

7. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to 5 claim 3 wherein the component (b) comprises a carbon black pigment dispersed in an acrylic or vinyl ether monomer or oligomer.

8. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to 10 claim 7 wherein the component (b) consists essentially of a carbon black pigment dispersed in a multifunctional acrylic monomer.

9. An ultraviolet radiation curable temporarily pressure-sensitive adhesive composition according to 15 claim 8 wherein said multifunctional acrylic monomer is trimethylolpropane triacrylate.

10. An ultraviolet radiation curable temporarily pressure-sensitive adhesive composition according to 20 claim 1 or claim 3 wherein the component (c) is 4-hydroxybutyl vinyl ether.

11. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 1 or claim 3 wherein component (a) is present in an amount ranging from 50.0% to 60.0% by weight.

25 12. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 3 which gives an optical density greater than about 1.4, wherein component (b) is present in an amount ranging from 11.0% to 15.0% by weight and

- 31 -

wherein the pigment concentration is present in an amount ranging from 2.2% to 3.0% by weight of the total composition.

5 13. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 1 or claim 3 wherein component (c) is present in an amount ranging from 25.0% to 35.0% by weight, based on the total composition.

10 14. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 2 or claim 4 wherein the component (d) is an acetophenone derivative which is 2-hydroxy-2-methyl-1-phenyl propan-1-one, or diethoxyacetophenone, or a blend of said acetophenone derivative with a 15 thioxanthone and an amine benzoate or 2-benzyl-2-(dimethylamino)-1-(4-(4-morpholinyl)phenyl)-1-butanone.

20 15. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 2 or claim 4 wherein the component (e) is a metallic triarylsulfonium salt of hexafluorophosphate.

25 16. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 2 or claim 4 wherein component (d) is employed in an amount ranging from 1% to 6% by weight, based on the composition.

17. An ultraviolet radiation-curable temporarily pressure-sensitive adhesive composition according to claim 2 or claim 4 wherein component (e) is employed

WO 94/13749

PCT/CAS/00519

- 32 -

in an amount ranging from 0-2% by weight, based on the composition, and in an amount ranging from 0 - 6% by weight, based on component (c).

18. A method of providing a substrate with indicia, which comprises:

- 5 (1) forming a laminate of
 - (a) a polyester film having a thickness of 12-25 microns;
 - (b) a release coating of a thickness of 1-2
 - 10 (c) a protective layer 1-2 microns thick;

and

(d) a stack of dielectric and/or metal layers having a maximum thickness of 1 micron;

15 (2) providing said substrate with a plurality of areas, each bearing a pressure sensitive adhesive as defined in claim 3;

20 (3) subjecting said substrate containing said adhesive-bearing areas to ultraviolet radiation to render said area tacky;

25 (4) bringing the outer surface of said stack of dielectric and/or metal layers into pressurized contact with said adhesive-bearing areas on said substrate, thereby adhering said laminate to said area on said substrate; and

(5) stripping said laminate away from the substrate, whereby the dielectric and metal layers are sheared from the release coating and firmly adhere to said areas on said substrate.

30 19. A method according to claim 18 wherein the substrate is banknote paper.

20. A method according to claim 19 wherein

WO 94/13749

PCT/CAN/00519

- 33 -

method step (2) is effected by offset gravure printing, said printing providing said banknote paper with a pattern of adhesive patches thereon.

21. An article of manufacture comprising:
5 a substrate, to selected areas on the surface of which is permanently bonded a semi-transparent dielectric material, said bonding being by means of a black pressure-sensitive adhesive curable at ambient temperatures by ultraviolet radiation, said adhesive being as defined in claim 3.
- 10
22. An article of manufacture according to claim 21 which comprises a pattern of patches of a semi-transparent dielectric material and/or a very thin layer of metal, permanently bonded to banknote paper by means of said pressure-sensitive adhesive.
- 15

WO 94/13749

PCT/CA93/00519

1/2

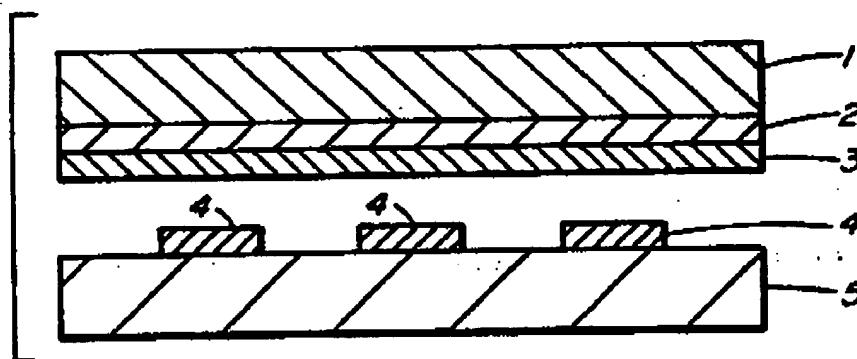


FIG. 1

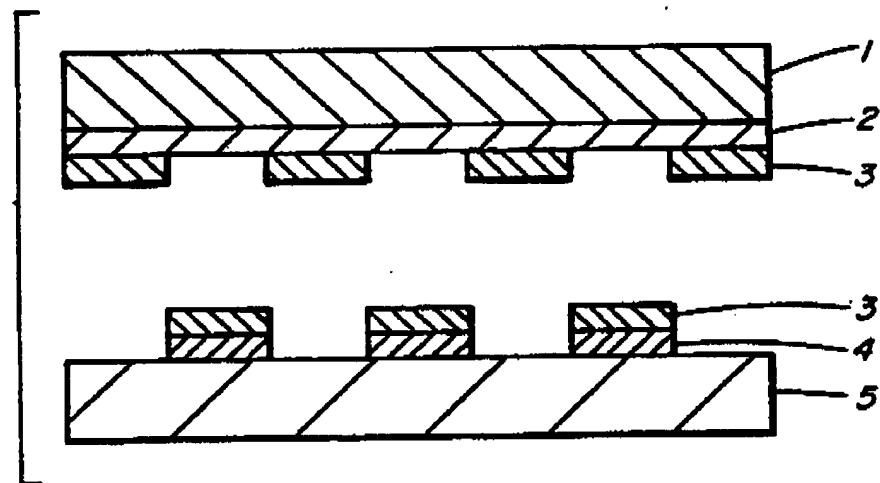


FIG. 2

WO 94/13749

PCT/CA93/00519

2/2

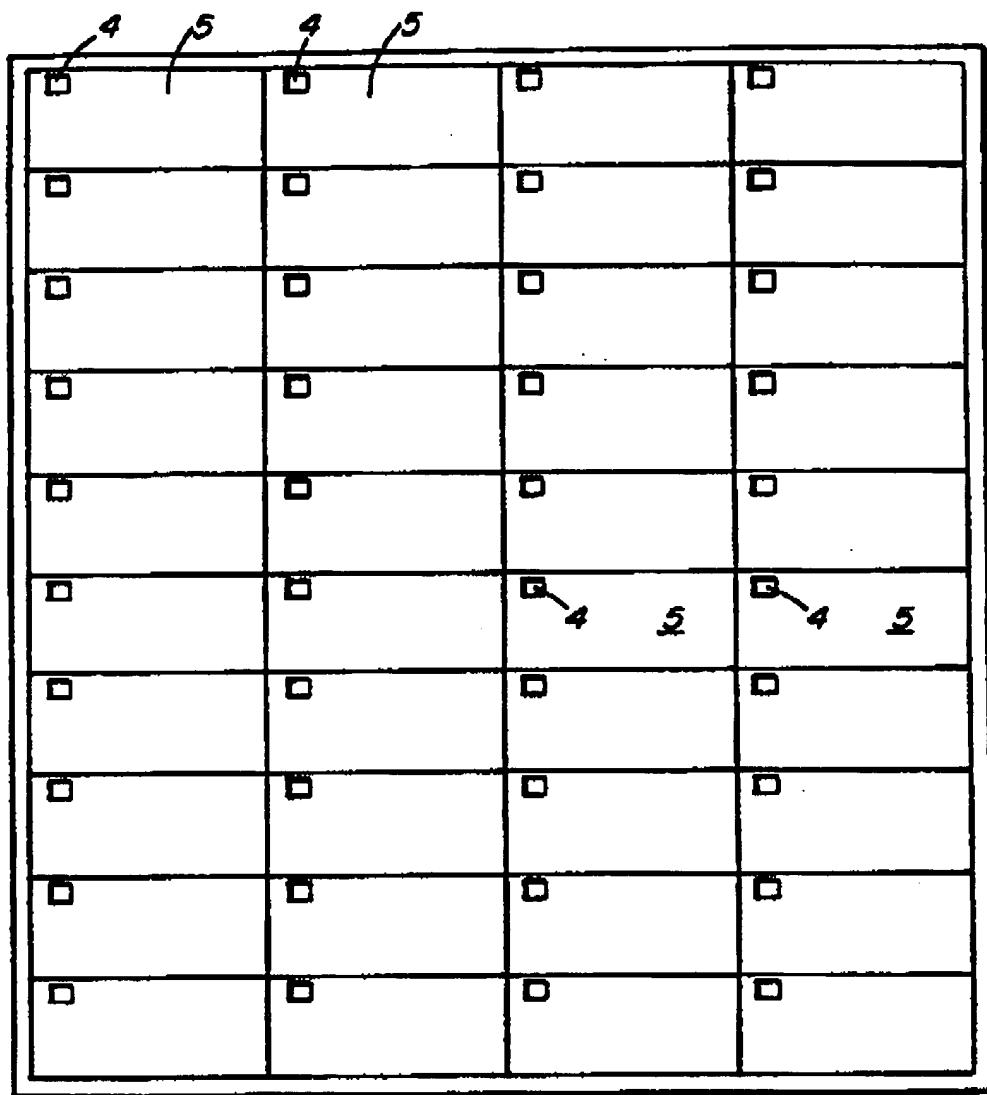


FIG. 3

INTERNATIONAL SEARCH REPORT

Int'l. Appl. No.
PCT/CA 93/00519A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09J4/06 C09J167/07

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (Classification system followed by classification symbols)
IPC 5 C09J C09D C08F B41M B42D G03F D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data bases consulted during the international search (names of data bases and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO,A,93 05124 (BANK OF CANADA) 18 March 1993 see the whole document	1-22
Y	FR,A,2 039 538 (PPG INDUSTRIES) 15 January 1971 see page 2, line 6 - page 3, line 4 see page 15, line 25 - line 38 see page 22, line 15 - line 40	1-6, 11, 16, 17
Y	US,A,4 368 300 (NAKANO ET AL.) 11 January 1983 see claims 1,26	1-6, 11, 16, 17
A	EP,A,0 486 065 (GAI GESELLSCHAFT FÜR AUTOMATION UND ORGANISATION) 20 May 1992 -/-	1-4, 18-20

 Further documents are listed in the continuation of box C. Patent family numbers are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *B* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claimed or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other source
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *M* document member of the same patent family

Date of the actual completion of the international search 8 March 1994	Date of mailing of the international search report 18.03.94
Name and mailing address of the ISA European Patent Office, P.O. 5018 Potsdam 3 NL - 2233 HV Lisse (Netherlands) Tel. (+31-70) 340-2040, Telex 31 651 epc nl. Fax (+31-70) 340-3016	Authorized officer Andriollo, G

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/CA 93/00519

C/(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant portion	Relevant to claim No.
A	US,A,4 705 300 (BERNING ET AL.) 10 November 1987	1-4,21, 22

2

Form PCT/ISA/210 (continuation of record sheet) (July 1992)

page 2 of 2

PAGE 43/44 * RCVD AT 2/21/2005 11:29:04 AM [Eastern Standard Time] * SVR:USPTO-EFXRF-1/0 * DNIS:8729306 * CSID:651 736 6133 * DURATION (mm:ss):12:30

INTERNATIONAL SEARCH REPORT
Information on patent family members

Int. Appl. No.
PCT/CA 93/00519

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9305124	18-03-93	AU-A-	1563892	05-04-93
FR-A-2039538	15-01-71	NONE		
US-A-4368300	11-01-83	JP-C- JP-A- JP-B-	1477025 57098521 63024528	27-01-89 18-06-82 20-05-88
EP-A-0486065	20-05-92	DE-A- CA-A-	4036637 2055621	21-05-92 17-05-92
US-A-4705300	10-11-87	US-A- US-A-	4779898 4930866	25-10-88 05-06-90